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Alkali-Carbonate Rock Reactions in Concrete: Developments in Specification and Control

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MISCELLANEOUS PAPER C-72-9

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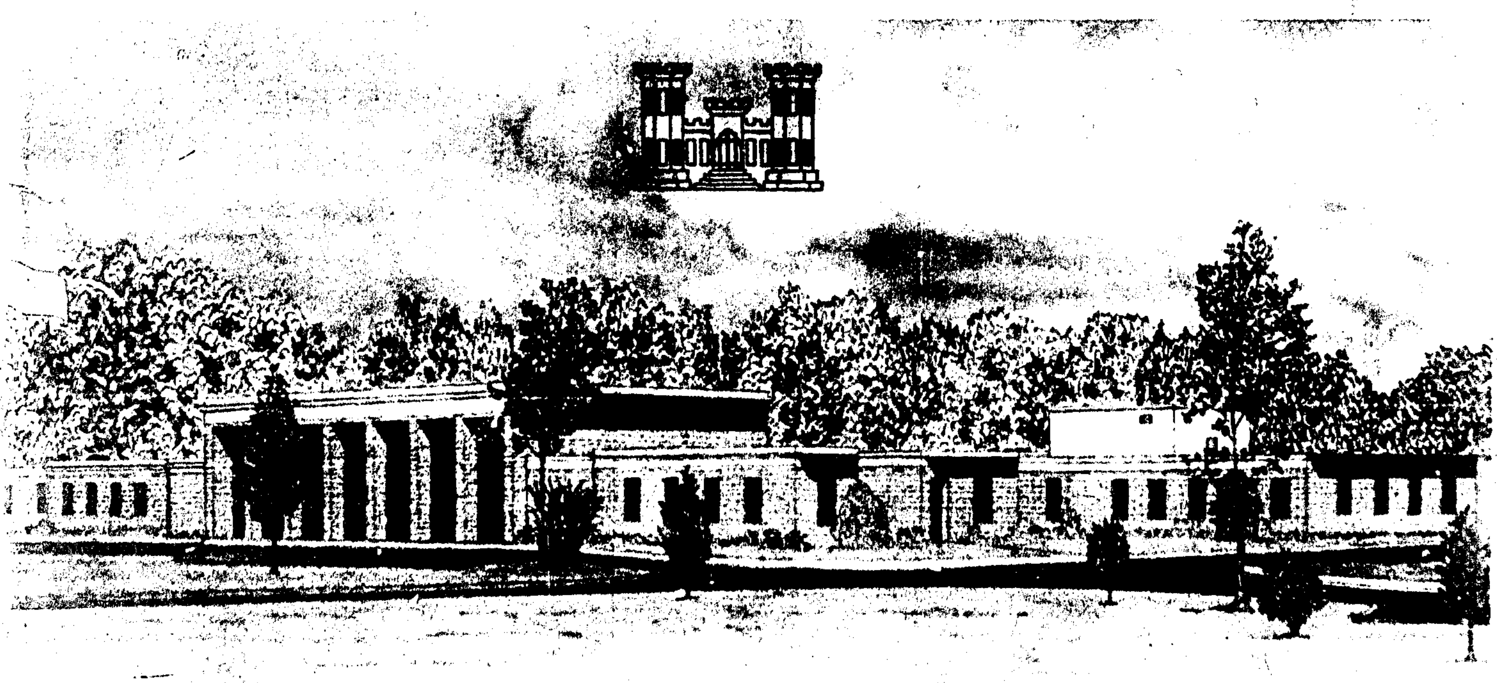
B. Mather



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Conducted by U. S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi

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FOREWORD

In November 1968 as part of the planning for an informal conference session to be held at the January 1969 meeting of the Highway Research Board, Mr. Howard H. Newlon asked Mr. Bryant Mather to prepare a discussion on "Developments in Specifications and Control." The session was entitled "Alkali-Carbonate Rock Reactions Revisited" and was intended to update the state-of-the-art as it had been reviewed in 1964 and published in HR Record No. 45. The discussion took place on 13 January 1969. In August 1971, Mr. Newlon's successor as chairman of the HRB Committee on Chemical Aspects of Concrete Durability (A2-E02), Mr. Carl F. Crumpton, requested Mr. Mather to update his notes from the 1969 discussion for consideration for publication. On 29 September 1971 the manuscript was submitted to OCE for clearance and was cleared on 19 October. It has been submitted to Mr. Crumpton for consideration by HRB.

The work reported in this paper was accomplished, in part, under OCE Civil Works Investigations Engineering Studies Item 603, "Cement-Aggregate Reaction."

Directors of the WES during the preparation of this paper were COL Levi A. Brown, CE, and COL Ernest D. Peixotto, CE. Technical Director was Mr. F. R. Brown.

DEVELOPMENTS IN SPECIFICATION AND CONTROL*

by

Bryant Mather**

At the 43rd Annual Meeting of the HRB in 1964, the Symposium on alkali-carbonate rock reactions was held--which later was the basis of Highway Research Record No. 45, containing 15 reports and bibliography. The bibliography listed 56 items. In so far as these dealt with specifications and control, they generally implied that aggregates of the sort that participated in the deleterious alkali-carbonate rock reaction should not be used. Presumably such exclusion would be based on service record if standard acceptance tests failed to yield a basis for rejection when results of such tests were compared with criteria such as those given in ASTM C 33. Indeed, the early work of Swenson (1957) on the rock from Kingston was presented primarily in terms of the fact that the rock had, by service record, been shown to be associated with deleterious expansion of concrete but would not be detected and classed as unacceptable by then current ASTM criteria. The work of Lemish and associates in Iowa, beginning in 1957, was largely associated with explaining the unsatisfactory service of concrete made using certain sources of carbonate rock aggregates.

Swenson and Gillott (1960) reported that the use of a cement of sufficiently low alkali content appeared to have provided a satisfactory solution in

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*For presentation at Conference Session on "Alkali-Carbonate Rock Reactions Revisited," Session No. 1, 48th Annual Meeting, HRB, 2:00 PM, 13 January 1969.

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the Kingston area. Hadley (1961) proposed the de-dolomitization reaction and petrographic criteria for the recognition of types of rock that were capable of participation therein.

Newlon and Sherwood (1962) reported results of a survey throughout Virginia in which rock from seven quarries was found to expand more than 0.2% in the rock prism test.

This essentially was the state-of-the-art with regard to specification and control in 1963 before the symposium.

In HR Record 45, we find Hadley writing (page 16) "simple test methods have been developed which permit rapid identification of expanding rocks and indicate their general level of reactivity." Swenson and Gillott, under the heading "Recommended Field Practice" (page 25), reiterated that expansion will be reduced to 'safe' values if the alkali content of the cement is held to 0.45 or less Na_2O equivalent. They also suggest dilution, attention to joints, and other details. Lemish and Moore indicated progress in detecting the features of rocks that are associated with poor service. Axon and Lind pointed out difficulties in correlating petrographic and performance data and report that rock from one quarry was not approved because the concrete showed excessive expansion but none had yet been rejected because of expansion in the prism test. Peter Smith presented the results of his experience in "Learning to Live With a Reactive Carbonate Rock." The precautions required included: (1) Selective quarrying and removal of unacceptable material based on service records and tests to an age of 84 days with an expansion of 0.05% or more in a concrete prism made using a cement with more than 1.1% alkalies.

(2) A vapor barrier was installed below the pavement. (3) Expansion joints were provided to a greater extent than normally done. Newlon and Sherwood suggested dilution and reduction of cement alkalies to 0.40% maximum in some cases. They proposed an expansion in concrete of 0.03 percentage points above the control as indicative of reactive aggregate.

Since 1964 there has been considerable progress in various agencies.

In ASTM Committee C-9, the rock prism test has been standardized and published as Designation: C 586-66T. This says--with a variety of qualifying comments--that a rock prism that expands more than 0.10 percent is reactive rock. A letter ballot was canvassed on 10 January 1969 on advancing this method to standard*.

At the last meeting of Subcommittee II-b of C-9 (December 1968), there was discussion of publication of the results of a cooperative study of the use of the mortar-bar test (C 227) on reactive carbonate aggregates. References are now included in C 227** regarding the lower level of expansion found when this test is used on reactive carbonate rocks as contrasted with the higher levels obtained when used with an equally reactive siliceous rock.

In December 1968, Committee C-9 accepted, subject to letter ballot, a revision of the specifications for concrete aggregate C 33 setting, for the first time, criteria on reactive carbonate rocks in the ASTM aggregate specifications. This, in effect, says a reactive carbonate rock is one that shows 0.1% or more expansion in 84 days or less. Since this proposal was not approved on the letter ballot, the provisions mentioned do not now appear in C 33. They are, therefore, given below:

*Now C 586-69 (effective 3 October 1969).

**C 227-69 is the current version.

The Subcommittee approved, subject to letter ballot, the following revisions to the "Standard Specifications for Concrete Aggregates," Designation: C 33-67:

10.1.15 Reactive Aggregates: add "ASTM Method C 586-66T, Tentative Method of Test for Potential Reactivity of Carbonate Rocks for Concrete Aggregates (Rock Cylinder Method)."

Appendix, A1.1: preface the existing test with the following:

"Two types of alkali reactivity are recognized: (1) an alkali-silica reaction involving certain rocks, minerals, and artificial glasses, and (2) an alkali-carbonate reaction involving some carbonate rocks, usually calcitic dolomites and dolomitic limestones."

Appendix, A1.1.1: amend the first sentence to read, "Certain siliceous materials are known to be reactive with the alkalies in cement."; add the following paragraph to the section:

"Fine-grained dolomites, calcitic dolomites, or dolomitic limestones, especially those in which the dolomite crystals are enclosed in a matrix of clay and finely disseminated calcite, should be considered potentially alkali-reactive."

Add the following section to the Appendix:

"A1.1.5 ASTM Method C 586, Tentative Method of Test for Potential Reactivity of Carbonate Rocks for Concrete Aggregates (Rock Cylinder Method) -- Rock types represented by specimens expanding 0.1 percent in 84 days or less of immersion in NaOH solution should be considered suspect, and their performance in concrete evaluated."

Meanwhile, in the Corps of Engineers, steps were being taken to revise "Appendix II" on "Evaluating Reactive Aggregates" in the Engineer Manual 1110-2-2000, "Standard Practice for Concrete." This appendix, as adopted in 1965, covered only materials capable of participation in the alkali-silica reaction. The revisions were begun in 1967, modified in draft in 1968 (and the Manual is scheduled for publication including the revised Appendix II in 1971). Since this document has not been widely circulated, it is given below:

APPENDIX II:

EVALUATING REACTIVE AGGREGATES

ALKALI-SILICA REACTION

1. CRITERIA FOR RECOGNITION OF POTENTIALLY DELETERIOUS CONSTITUENTS IN AGGREGATE. Detailed criteria for the recognition of potentially deleterious siliceous constituents in aggregates are given in ASTM Proceedings (see ref 4b). These may be summarized as follows:

a. Opal. Opal may occur in igneous, sedimentary, or metamorphic rocks; in veins, cavity fillings, or linings; as a replacement as in petrified wood; or as the cementing material of sandstone. Opal consists of amorphous silica with varying amounts of water; its index of refraction is usually about 1.45, seldom higher than 1.46 or lower than 1.40.

b. Chalcedony. Chalcedony is most frequently found as a constituent of chert either when the chert is included in a carbonate rock or makes up sand and gravel particles. Chalcedony consists of material having the properties of quartz except that it has a lower specific gravity; its index of refraction is lower than the lowest index of quartz (1.544).

c. Tridymite and Cristobalite. These are high-temperature crystalline forms of silica found in igneous rocks such as andesite and rhyolite.

d. Acid and Intermediate Volcanic Glass. Acid glasses contain more than 65% silica; intermediate glasses contain between 55 and 65%. Glasses with more than 55% silica generally have an index of refraction lower than 1.57.

2. RELIABILITY OF METHODS. The following test methods are included in reference 2b(1) of the main text*:

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*Handbook for Concrete and Cement, Waterways Experiment Station, Vicksburg, Miss.

CRD-C 123 Method of Test for Length Change of Mortar Bars Caused by Reactivity of Aggregates with Alkalies in Portland Cement (= ASTM C 227)

CRD-C 127 Method of Petrographic Examination of Aggregates for Concrete (= ASTM C 295)

CRD-C 128 Method of Test for Potential Reactivity of Aggregates (Chemical Method) (= ASTM C 289)

In spite of improvements in the available test methods which have resulted from continuing research and development, none of the available means of evaluation can be relied upon independently, or collectively, to provide an unquestionably positive answer to the problem of potentially harmful reactivity of an aggregate whose constituents include materials capable of reacting with the alkalies in portland cement. The results of petrographic examination with corroborating evidence from the mortar-bar tests are considered the most reliable means of evaluating potential reactivity. It may be anticipated that because interpretation is involved in using the results of petrographic examinations and because the mortar-bar test is not as reproducible as would be desirable, contradictions will sometimes occur between the indications yielded by the two methods. It is for this reason that results from the two methods should be considered together. Spurious results are possible with the chemical test when certain substances are present in the aggregate being tested. The test, however, can be of value when interpreted in the light of petrographic data and should be used together with the results of petrographic examination. The main value of the chemical test lies in the early availability of results. Finally, all three of the methods must be considered as indices that provide information to which engineering judgment must be applied in arriving at a rational solution of the problem of potential reactivity as it relates to any particular aggregate. All possible information including geological appraisal of a source, service records when they can be dependably established, and results of tests and petrographic examination are essential to a proper solution of the problem.

3. CRITERIA FOR EVALUATING POTENTIAL REACTIVITY.

a. General. The fine and coarse aggregates for use in any given concrete mixture will be evaluated separately for potential reactivity regardless of whether or not they come from the same or from different sources.

b. Petrographic Results. A fine or coarse aggregate will be evaluated as potentially deleteriously reactive if the petrographic examination reveals any of the following:

(1) The presence of any opal.

(2) More than 5% chert in which any chalcedony is detected.

(3) More than 3% glassy igneous rocks in which any acid or intermediate glass is detected.

c. Mortar-Bar Results. A fine or coarse aggregate will be evaluated as potentially deleteriously reactive if mortar bars made with cement containing not less than 1.0% alkalies calculated as Na_2O show more than 0.10% expansion at one year, or more than 0.05% expansion at six months. Any set of mortar bars that show an average expansion of 0.10% or more at any age should be regarded as having manifested excessive expansion, and the combination of materials used in making them should be regarded with suspicion. Sets of specimens showing an average expansion of more than 0.05% at six months but less than 0.10% at one year may usually be regarded as having been made with aggregates that are not deleteriously reactive. When the average expansion is close to these limits, assistance in evaluating its significance may be obtained from the slope and trend of the time-length change curves.

d. Quick-Chemical Results. A fine or coarse aggregate will be evaluated as potentially deleteriously reactive if the data point for it falls to the right of the line on the graph given in the test method.

e. Service Record. A fine or coarse aggregate will be evaluated potentially deleteriously reactive when service records establish that deleterious reactions have occurred in a structure in which the aggregate has been used. As indicated in paragraph 2, none of the laboratory methods can be relied on independently or collectively to provide an unquestionably positive indication of potentially harmful reactivity; consequently, service record data are of critical importance when they can be obtained. Every effort should be made to obtain data on performance in service of the aggregates in question, especially with cements of high-alkali content, and desirably in concrete exposed to similar conditions to those to which the proposed work will be exposed.

f. Blended Aggregates. In the event the coarse or fine aggregate for a project will be composed of a mixture of materials from two or more sources, the combined fine or combined coarse aggregate, in the grading intended for use, will be evaluated for potential reactivity. For the criteria applicable to the results of petrographic examination, the estimated amounts of potentially deleterious constituents present will be calculated by the method of weighted averages on the basis of the combined grading of the fine or coarse aggregate proposed for use on a project. For the mortar-bar test, the aggregate for use in the mortar shall be graded as prescribed in the test method. Where fine aggregate is to be composed of a blend of materials from two or more sources, each sieve fraction used in the test grading for mortar bars shall include material from each source proportional to the contribution of each source to the total amount of material in that size fraction of the job blend. For coarse aggregates, the crushed material from which the test grading for mortar bars is prepared shall include all the rock types occurring in the aggregates which will compose the job coarse aggregates in approximately the same proportions as they will occur in the job coarse aggregates. Similar procedures are applicable to selection and treatment of samples for the quick-chemical test.

g. Application of Criteria. It is preferable to have evaluations of each fine aggregate and each coarse aggregate based on service record, petrographic examination, mortar-bar tests, and quick-chemical tests. The decision as to whether an aggregate is potentially deleteriously reactive or not is readily made when all of the evaluations agree; however, as pointed out in paragraph 2 such will not always be the case. The criteria will, therefore, be applied as follows: The use of "low-alkali" portland cement meeting the requirements of Federal Specification SS-C-192 shall be required whenever either the fine aggregate or the coarse aggregate is evaluated as potentially deleteriously reactive either by service record, by petrographic examination results, or by mortar-bar test results. When service-record evaluation and mortar-bar evaluation are not available, the cement shall be low alkali whenever either the petrographic or the quick-chemical evaluations indicate potentially deleterious reaction. The evaluation as deleterious by the quick-chemical test may be disregarded only if evaluations as not deleterious are available from at least two of the three other methods of evaluation. When conflicting or inconclusive evaluations are obtained and time permits, new samples should be obtained and check evaluations made. When reasonable doubt exists, "low-alkali" cement should be required.

4. LITERATURE REFERENCES. The following is a selected list of references on the subject which will be of interest and value in connection with application of the criteria established hereby:

a. Lerch, William, "Chemical reactions." American Society for Testing Materials Special Technical Publication, No. 169 (1955), pp 334-345.

b. Mather, Bryant, "Petrographic identification of reactive constituents in concrete aggregate." Proceedings, American Society for Testing Materials, vol 48 (1948), pp 1120-1125.

c. Mielenz, R. C., "Evaluation of the quick chemical test for alkali reactivity of concrete aggregate." Highway Research Board Bulletin No. 171 (1958), pp 1-15.

d. U. S. Army Engineer Waterways Experiment Station, CE, Tests for Chemical Reactivity Between Alkalies and Aggregate; Quick-Chemical Test and Mortar-Bar Test. Technical Memorandum No. 6-368, Report Nos. 1 and 2, August 1953 and September 1956, respectively, Vicksburg, Miss.

ALKALI-CARBONATE ROCK REACTIONS

5. GENERAL STATEMENT. The results of studies that have been reported indicate that four types of alkali-carbonate rock reaction may be recognized in concrete. A thorough review of research through 1964 is contained in reference 8f. It is possible that future work will show that some of these are merely different manifestations of the same reaction, shown by different rocks under a variety of circumstances. The four types of reactions are discussed below:

a. Reactions Involving Non Dolomitic Carbonate Rocks. Some rocks which contain little or no dolomite may be reactive (ref 8a, b). The reaction is characterized by reaction rims which are visible along the borders of cross sections of aggregate particles; etching these cross-sectional surfaces with dilute hydrochloric acid reveals that the rims are 'negative' rims; that is, the reaction rim zone dissolves more rapidly than the interior of the particle. The evidence to date indicates that the reaction is not harmful to concrete and may even be beneficial.

b. Reactions Involving Dolomite or Highly Dolomitic Carbonate Rocks. The reaction of dolomite or highly dolomitic aggregate particles in concrete has been reported (ref 8c). The reaction was characterized by visible reaction rims on cross sections of the aggregate particles. When these cross-sectional areas of aggregate particles were etched with acid, the rimmed area dissolved at the same rate as the nonrimmed area. No evidence was reported that this reaction was damaging to concrete.

c. Reactions Involving Impure Dolomitic Carbonate Rocks. The rocks of this group have a characteristic texture and composition. The texture is such that larger crystals of dolomite are scattered in and surrounded by a fine-grained matrix of calcite and clay. The rock consists of substantial amounts of dolomite and calcite in the carbonate portion, with significant amounts of acid-insoluble residue consisting largely of clay. Two reactions have been reported with rocks of this sort, as follows:

(1) Dedolomitization Reaction. This reacion is believed to have produced harmful expansion of concrete (ref 8d). Magnesium hydroxide, brucite, ($Mg(OH)_2$), is formed by this reaction; its presence in concrete which has expanded and which contains carbonate aggregate of the indicated texture and composition is strong evidence that this reaction has taken place.

(2) Rim-Silicification Reaction. This reaction is not definitely known to be damaging to concrete, although there are some data which suggest that a retardation in the rate of strength development in concrete is associated with its occurrence. The reaction is characterized by enrichment of silica in the borders of reacted particles (ref 8e). This is seen as a positive or raised border at the edge of cross-sections of reacted particles after they have been etched in dilute hydrochloric acid. Reaction rims may be visible before the concrete surfaces are etched.

Fortunately, carbonate rocks that contain dolomite, calcite, and insoluble material in the proportions that cause either the dedolomitization or rim-silicification reactions are relatively rare in nature as major constituents of the whole product of an aggregate source.

6. CRITERIA FOR RECOGNITION OF POTENTIALLY HARMFULLY REACTIVE CARBONATE ROCKS. These criteria serve to indicate those dolomitic carbonate rocks capable of producing the dedolomitization or rim-silicification reaction. Since the reactions generated by some very dolomitic or by some nondolomitic carbonate rocks are not known to be harmful to concrete, no attempt is made to provide guides for recognition of these rocks at this time.

a. When petrographic examinations are made according to CRD-C 127 of quarried carbonate rock or of natural gravels containing carbonate-rock particles, adequate data concerning texture, calcite-dolomite ratio, the amount and nature of the acid-insoluble residue, or some combination of these parameters will be obtained in order to recognize potentially reactive rock. Rocks associated with observed expansive dedolomitization have been found to be characterized by fine grain size (generally 50 microns or less) with the dolomite largely present as small, nearly euhedral crystals generally scattered in a finer grained matrix in which the calcite is disseminated. The tendency to expansion, other things being equal, appears to increase with increasing clay content from about 5 to 25% by weight of the rock, and also appears to increase as the calcite-dolomite ratio of the carbonate portion approaches 1:1.

b. Samples of rock recognized as potentially reactive by petrographic examination will be tested for length change during storage in alkali solution in accordance with CRD-C 146 (ASTM Designation: C 586). Rock characterized by expansion of 0.1% or more by or during 84 days of test by CRD-C 146 shall be classified as potentially reactive.

c. If adequate reliable data are available to demonstrate that concrete structures containing the same aggregate have exhibited deleterious reactions, the aggregate shall be classified as potentially reactive on the basis of its service record.

7. APPLICATION OF CRITERIA. The application of engineering judgment will be required in making the final decision as to which rocks are to be classified as innocuous and which are to be classified as potentially reactive. Once a rock has been classified as potentially reactive, the action to be taken should be as indicated in the following subparagraphs.

a. Avoid use as aggregate of rock classified as potentially reactive by appropriate procedures such as selective quarrying.

b. If it is not feasible to avoid the use of rock classified as potentially reactive, then specify the use of low-alkali cement, the minimum aggregate size that is economically feasible, and dilution so that the amount of potentially reactive rock does not exceed 20% of the coarse aggregate, or 20% of the fine aggregate, or 15% of the total aggregate in cases where there is potentially reactive rock in both the coarse and fine aggregate.

c. If it is not practical to enforce conditions a or b, then the aggregate source which contains potentially reactive rock shall not be indicated as a source from which acceptable aggregate may be produced.

7. LITERATURE REFERENCES. The following references contain descriptions of the various types of alkali-carbonate rock reaction:

a. U. S. Army Engineer Waterways Experiment Station, CE, Aggregate Investigations - Milford Dam, Kansas - Examination of Cores from Concrete Structures. Technical Report No. 6-629, Vicksburg, Miss., June 1963.

b. ________________, Investigation of a Reaction Involving Nondolomitic Limestone Aggregate in Concrete, by Alan D. Buck, Miscellaneous Paper 6-724, Vicksburg, Miss., June 1965.

c. ________________, Results of Laboratory Tests and Examinations of Concrete Cores, Carlyle Reservoir Spillway, Carlyle, Illinois, by W. O. Tynes, W. I. Luke, and B. J. Houston, Miscellaneous Paper No. 6-802, Vicksburg, Miss., March 1966.

d. Hadley, D. W., Alkali reactivity of carbonate rocks--expansion and dedolomitization. Proceedings, Highway Research Board, vol 40 (1961), pp 462-474, 664.

e. Bisque, R. E., and Lemish, John, Chemical characteristics of some carbonate aggregate as related to durability of concrete. Highway Research Board Bull. 196, Washington, D. C. (1958), pp 29-45.

f. Highway Research Board, "Symposium on Alkali-Carbonate Rock Reactions." Highway Research Record No. 45, HRB Publication 1167 (1964). 244 pp.

Following the development of the criteria given in the revised Appendix II, the selection of which was based primarily on published work done elsewhere than in the Corps of Engineers, the Waterways Experiment Station undertook an investigation having as its purpose the development of data that would verify or permit modification or refinement of these criteria for permissible expansion, time, and dilution. This program is still in progress.